

Taichi KOBAYASHI, et al. U.S. Appln. No.: 10/696,312 Attorney Docket No.: Q78246 Date Filed: October 30, 2003 1 of 2

#### DECLARATION

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Dated this 22nd day of June 2005

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[DOCUMENT NAME] Specification [TITLE OF THE INVENTION] Near-infrared absorption film [Scope of Claim for a Patent] [Claim 1]

A near-infrared absorption film, comprising:

a transparent substrate; and

a near-infrared absorption layer which comprises a layer comprising a cyanine compound represented by the formula (1); and a layer comprising a diimonium compound,

Formula (1)

[Chemical Formula 1]

$$H_3C$$
 $CH_3$ 
 $H_3C$ 
 $CH_3$ 
 $A$ 
 $CH$ 
 $N$ 
 $N$ 
 $R^1$ 
 $R^2$ 
 $X$ 

wherein, in the formula (1), "A" is a divalent bonding group comprising an ethylene group. " $R^{1"}$  and " $R^{2"}$  are monovalent groups comprising carbon atoms. "X-" is a monovalent anion. [Claim 2]

The near-infrared absorption film according to Claim 1, wherein "A" is represented by any one of the formulae (2) to (4): [Chemical Formula 2]

$$-(CH = C)_3 -, -CH = CH - CH -, -CH = CH - CH -$$
Formula (2) Formula (3) Formula (4)

wherein, in formulae (2) to (4), "Y" is any one of an alkyl group, diphenylamino group, halogen atom and hydrogen atom.

[Claim 3]

The near-infrared absorption film according to Claim 1 or 2,

wherein the near-infrared absorption layer comprises a quencher compound.

[Claim 4]

The near-infrared absorption film according to Claim 3, wherein the quencher compound is any one of a metal compound comprising a structure represented by any one of the formulae (5) and (6), and an aminium compound comprising a structure represented by the formula (7).

[Chemical Formula 3]

wherein, in the formulae (5) and (6), "M" is any one of Ni, Cu, Co, Pt and Pd.

[Chemical Formula 4]

$$\begin{bmatrix} R^{3} \\ R^{4} \end{bmatrix} N - \begin{bmatrix} R^{5} \\ R^{6} \end{bmatrix}^{1+} \cdot X^{-}$$
Formula (7)

wherein, in the formula (7), " $R^{3}$ " to " $R^{6}$ " are any one of an alkyl group, an aryl group, a group comprising an aromatic ring, a hydrogen atom and a halogen atom. " $X^{-1}$ " is any one of I-, Br-, ClO<sub>4</sub>-, BF<sub>4</sub>-, PF<sub>6</sub>-, SbF<sub>6</sub>-, CH<sub>3</sub>SO<sub>4</sub>-, NO<sub>3</sub>-, and CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-SO<sub>3</sub>-. [Claim 5]

The near-infrared absorption film according to Claim 3 or Claim 4, wherein the quencher compound is represented by any one of the formulae (8) to (10).

[Chemical Formula 5]

$$\begin{bmatrix} (t)Bu & S & S & Bu(t) \\ S & S & S & \end{bmatrix}^{-} (n)Bu_4N^{+}$$
Formula (8)

$$\left[\begin{array}{c|c} O_2 \\ S \\ S \\ S \\ O_2 \end{array}\right]^{-} \quad \text{(n)Bu}_4 N^+$$
Formula (9)

#### [Claim 6]

The near-infrared absorption film according to any one of Claim 3 to Claim 5, wherein the layer comprising the cyanine compound comprises a quencher compound represented by any one of the formulae (7) and (10), and the layer comprising the diimonium compound comprises a quencher compound represented by any one of the formulae (8) and (9).

#### [Claim 7]

The near-infrared absorption film according to any one of Claim 1 to Claim 6, wherein the diimonium compound is represented by any one of formulae (I) and (II).

[Chemical Formula 6]

$$\begin{bmatrix} R_8^7 \\ R_8 \end{bmatrix} N \longrightarrow N < \begin{bmatrix} R_1^9 \\ R_{10} \end{bmatrix}^{2+} \cdot 2X$$
 (1)

$$\begin{bmatrix} R^{7} \\ R^{8} \end{bmatrix} N \longrightarrow \begin{bmatrix} N \\ R^{10} \end{bmatrix}^{2+} \cdot Y^{2-}$$
 (II)

wherein, in the formulae (I) and (II), " $R^{7}$ " to " $R^{10}$ " are any one of an alkyl group, an aryl group, a group comprising an aromatic ring, a hydrogen atom and a halogen atom. " $X^{-1}$ " is a monovalent anion, and " $Y^{2-1}$ " is a divalent anion.

[Claim 8]

The near-infrared absorption film according to any one of Claim 1 to Claim 7, wherein an amount of the cyanine compound is within the range of 0.1 parts by weight to 50 parts by weight relative to 100 parts by weight of the diimonium compound.

[Detailed Description of the Invention] [0001]

[Technical Field to which the Invention Belongs]

The present invention relates to especially a near-infrared absorption film suitable for disposing on a front surface of a plasma display (PDP).

[0002]

[Prior Art]

In the related art, in general, in electromagnetic wave shield optically transmitting materials disposed on the front surfaces of plasma displays (PDP), a near-infrared ray absorption film which absorbs near-infrared rays that cause malfunctions of other peripheral electronic equipment, is affixed to the PDP side of the display. It is required that this near-infrared absorption film has a high selective near-infrared absorbing ability to effectively block near-infrared rays while having excellent visible light transparency and tone.

[0003]

In order to satisfy the above requirements, various near-infrared

absorption films have been studied and proposed in Japanese Patent Application Laid-Open (JP-A) Nos. 09-230134, 10-78509 and 11-316309, but due to technical developments in recent years, infrared absorption films with still higher near-infrared ray blocking power, superior visible light transparency and better appearance have come to be required. [0004]

[Problems that the Invention is to Solve]

The present invention answers to the needs of the prior art and accomplish the following objects. Namely, the object of the present invention is to provide a near-infrared absorption film having an excellent near-infrared ray blocking performance and visible light transparency, an excellent tone, and durability such as anti-deterioration properties.

[0005]

[Means for Solving the Problems]

The means for solving the above-mentioned problems is as followings, namely, <1> a near-infrared absorption film comprises a transparent ("transparence" refers to transparence to "visible light", hereafter idem) substrate, and a near-infrared absorption layer which comprises a layer comprising a cyanine compound represented by formula (1), and a layer comprising a diimonium compound.

Formula (1)

[0006] [Chemical Formula 7]

[0007]

In the formula (1), "A" is a divalent bonding group comprising an ethylene group. " $R^{1}$ " and " $R^{2}$ " are monovalent groups comprising carbon atoms. "X-" is a monovalent anion. [0008]

<2> The near-infrared absorption film according to the above-mentioned <1>, wherein "A" is represented by at least any one of the formulae (2) to (4):
[0009]

[Chemical Formula 8]

[0010]

In formulae (2) to (4), "Y" is any one of an alkyl group, diphenylamino group, halogen atom and hydrogen atom.
[0011]

<3> The near-infrared absorption film according to the above-mentioned <1> or <2>, wherein the near-infrared absorption layer comprises a quencher compound.

<4> The near-infrared absorption film according to the above-mentioned <3>, wherein the quencher compound is any one of a metal compound comprising a structure represented by any one of the formulae (5) and (6), and an aminium compound comprising a structure represented by the formula (7).
[0012]

[Chemical Formula 9]

[0013]

In the formulae (5) and (6), "M" is at least any one of Ni, Cu, Co, Pt and Pd.

#### [0014]

[Chemical Formula 10]

$$\begin{bmatrix} R^3 \\ R^4 \end{bmatrix} N - \begin{bmatrix} R^5 \\ R^6 \end{bmatrix}^{1+} \cdot X^{-1}$$
Formula (7)

[0015]

In the formula (7), " $R^{3}$ " to " $R^{6}$ " are at least any one of an alkyl group, an aryl group, a group comprising an aromatic ring, a hydrogen atom and a halogen atom. " $X^{-1}$ " is any one of I-, Br-, ClO<sub>4</sub>-, BF<sub>4</sub>-, PF<sub>6</sub>-, SbF<sub>6</sub>-, CH<sub>3</sub>SO<sub>4</sub>-, NO<sub>3</sub>-, and CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-SO<sub>3</sub>-. [0016]

<5> The near-infrared absorption film according to the above-mentioned <3> or <4>, wherein the quencher compound is represented by at least any one of the formulae (8) to (10).
[0017]

[Chemical Formula 11]

$$\begin{bmatrix} (t)Bu & S & S & Bu(t) \\ S & S & S & Bu(t) \end{bmatrix}^{-}$$
 (n)Bu<sub>4</sub>N<sup>+</sup> Formula (8)

[0018]

<6> The near-infrared absorption film according to any one of the above-mentioned <3> to <5>, wherein the layer comprising the cyanine compound comprises a quencher compound represented by at least any one of the formulae (7) and (10), and the layer comprising the diimonium compound comprises a quencher compound represented by at least any one of the formulae (8) and (9).

<7> The near-infrared absorption film according to any one of the above-mentioned <1> to <6>, wherein the diimonium compound is represented by at least any one of formulae (I) and (II).
[0019]

[Chemical Formula 12]

$$\begin{bmatrix} R_8^7 \\ R^8 \end{bmatrix} N \longrightarrow N < \begin{bmatrix} R_1^9 \\ R^{10} \end{bmatrix}^{2+} \cdot 2X^{-}$$
 (1)

$$\begin{bmatrix} R^{7} \\ R^{8} \end{bmatrix} N \longrightarrow \begin{bmatrix} N \\ R^{10} \end{bmatrix}^{2+} \cdot Y^{2-}$$
 (II)

[0020]

In the formulae (I) and (II), "R<sup>7</sup>" to "R<sup>10</sup>" are at least any one of an alkyl group, an aryl group, a group comprising an aromatic ring, a hydrogen atom and a halogen atom. "X-" is a monovalent anion. "Y<sup>2</sup>-" is a divalent anion.

<8> The near-infrared absorption film according to any one of the above-mentioned <1> to <7>, wherein an amount of the cyanine compound is within the range of 0.1 parts by weight to 50 parts by weight relative to 100 parts by weight of the diimonium compound.
[0021]

[Mode for Carrying Out the Invention]

The near-infrared absorption film of the present invention comprises a transparent substrate, and a near-infrared absorption layer, and other layers if required.

[0022]

[Near-infrared absorption layer]

The near-infrared absorption layer comprises a layer comprising the cyanine compound and a layer comprising the diimonium compound, and other layers if required. [0023]

In the near-infrared absorption layer, as mentioned above, it is required that the cyanine compound and diimonium are contained in separate layers for the following reasons [1] to [3].

- [1] As both the cyanine compound and the diimonium compound comprise counter anions, by containing these moieties in separate layers, it is unnecessary to provide counter anions. As a result, there is a larger degree of freedom of combinations of the cyanine compound and diimonium compound.
- [2] The quencher compounds (antidegradant components) which act more effectively due to the cyanine compound and diimonium compound, mutually differ. For this reason, by providing separate layers comprising the cyanine compound and diimonium compound, the quencher compound which acts more effectively can be used for each layer, and the material excels in durability.
- [3] If the cyanine compound and diimonium compound are made to coexist in the same layer, degradation of the diimonium compound is accelerated. Therefore, by providing separate layers comprising these moieties, accelerated degradation of the diimonium compound can be avoided, and the material excels in durability.

  [0024]

-Cyanine compound-containing layer-

The cyanine compound is represented by the formula (1).

Formula (1)

[0025]

[Chemical Formula 13]

[0026]

In the formula (1), "A" is a divalent bonding group comprising an ethylene group. " $R^{1"}$ " and " $R^{2"}$ " are monovalent groups comprising carbon atoms. "X-" is a monovalent anion. [0027]

It is preferred that "A" in the formula (1) is represented by at least any one of the following formulae (2) to (4) from the viewpoint that they give the film an excellent near-infrared ray blocking performance, excellent visible light transparency and excellent tone.

[0028]

[Chemical Formula 14]

$$-(CH = C)_3$$
,  $-CH = CH$   $-CH = CH$   $-CH = CH$  Formula (2) Formula (3) Formula (4)

In formulae (2) to (4), "Y" is any one of an alkyl group, diphenylamino group, halogen atom and hydrogen atom.
[0029]

In formula (1), a specific example of the case where "A" is formula (3) is shown by formula (12), a specific example of the case where "A" is formula (4) is shown by the formula (13), and a specific example of the case where "A" is formula (2) is shown by formula (14), respectively. [0030]

[Chemical Formula 15]

$$H_3C$$
 $CH_3$ 
 $CH=CH$ 
 $CH-CH$ 
 $R^1$ 
 $R^2$ 
 $CH_3$ 
 $R^2$ 
 $X$ 

Formula (12)

$$H_3C$$
 $CH_3$ 
 $CH=C)_3$ 
 $CH=C)_3$ 
 $CH=C$ 
 $R^1$ 
 $R^2$ 
Formula (14)

[0031]

In formula (1), "R¹" and "R²" may be an alkyl, an aryl, an alkoxy, an alkoxycarbonyl, a sulfonylalkyl, a cyano, and the like. "X-" may be I-, Br-, ClO<sub>4</sub>-, BF<sub>4</sub>-, PF<sub>6</sub>-, SbF<sub>6</sub>-, CH<sub>3</sub>SO<sub>4</sub>-, NO<sub>3</sub>-, CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-SO<sub>3</sub>-, and the like. [0032]

The amount of the cyanine compound is preferably 0.1 parts by weight to 50 parts by weight, and more preferably 1 part by weight to 50 parts by weight, relative to 100 parts by weight of the diimonium compound described later.

If this amount is less than 0.1 parts by weight, near-infrared blocking properties may be insufficient, and if it is more than 50 parts by weight, visible light transparency may be insufficient.

[0033]

The layer comprising the cyanine compound can be made to contain various other components if desired. Among these other components, quencher compounds are preferred from the viewpoint that

oxidation of the cyanine compound is prevented, and a near-infrared absorption film with high durability is obtained.

[0034]

There is no particular limitation on the quencher compound, but in order to more easily prevent oxidation of the cyanine compound and obtain a near-infrared absorption film having excellent durability, it is preferably at least any one or both of a metal compound comprising a structure represented by at least any one of the formula (5) and the formula (6), and an aminium compound comprising the structure represented by the formula (7).

[Chemical Formula 16]

[0036]

In the formulae (5) and (6), "M" is at least any one of Ni, Cu, Co, Pt and Pd.

Formula (6)

[0037]

[Chemical Formula 17]

$$\begin{bmatrix} R^3 \\ R^4 \end{bmatrix}^{1+} \cdot X^{-}$$
Formula (7)

[0038]

In the formula (7), " $R^{3}$ " to " $R^{6}$ " are at least any one of an alkyl group, an aryl group, a group comprising an aromatic ring, a hydrogen atom and a halogen atom. " $X^{-1}$ " is any one of I-, Br-, ClO<sub>4</sub>-, BF<sub>4</sub>-, PF<sub>6</sub>-, SbF<sub>6</sub>-, CH<sub>3</sub>SO<sub>4</sub>-, NO<sub>3</sub>-, and CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-SO<sub>3</sub>-. [0039]

The metal compound comprising the structure represented by the

formula (5) may be a 1,2-benzene thiol-copper complex, 1,2-benzene thiol nickel complex or a bis-dithio benzyl nickel complex, but the metal compounds comprising the structure represented by the formulae (8) to (10) are more preferred from the viewpoint of anti-oxidation and durability.

[0040]

[Chemical Formula 18]

$$\left[\begin{array}{c|c} O_2 \\ S \\ S \\ S \\ O_2 \end{array}\right]^- \quad \text{(n)} Bu_4 N^+$$
Formula (9)

[0041]

As the metal compound comprising the structure shown by the formula (6), the metal complex comprising the structure represented by the formula (11) is more preferred from the viewpoint of anti-oxidation and durability.

[0042]

[Chemical Formula 19]

$$CH_3$$
 N-C-S-Cu-S-C-N $CH_3$  Formula (11)

[0043]

Among the above-mentioned quencher compounds, the quencher compounds represented by the formula (5) and the formula (7) are preferred from the viewpoint of durability improvement, and among the quencher compounds represented by the formula (5), the quencher compound represented by the formula (10) is particularly preferred. [0044]

The amount of the quencher compound in the above-mentioned near-infrared absorption layer is preferably 0.1 parts by weight to 1000 parts by weight, more preferably 1 part by weight to 500 parts by weight and still more preferably 1 part by weight to 100 parts by weight, relative to 100 parts by weight of the above-mentioned cyanine compound. [0045]

If the amount thereof is less than 0.1 parts by weight, durability improvements such as heat resistance, anti-oxidation properties and moisture resistance may not be sufficient, and if it is more than 1000 parts by weight, the near-infrared absorption layer may develop a coloration and the appearance of the near-infrared absorption film may be impaired.

[0046]

Examples of other components contained in the layer comprising the above-mentioned cyanine compound in addition to the quencher compound are various binder resins, near-infrared absorption agents other than the cyanine compound (e.g., near-infrared absorption agents such as phthalocyanines, nickel complexes, azo compounds, polymethine compounds, diphenylmethanes, triphenylmethanes, quinines and the like), antioxidants other than the quencher compound (e.g., antioxidants such as phenols, amines, hindered phenols, hindered amines, sulfur compounds, phosphoric acids, phosphorous acids, metal complexes, and the like), ultraviolet absorbers, colorants to improve the appearance of the film, pigments, dyes, and the like.

[0047]

The binder resin may be a homopolymer or a copolymer of polyester resin, acrylic resin, methacrylic resin, urethane resin, silicone resin, phenol resin, (meth)acrylic acid ester and the like. Among these, from the viewpoint that dispersion of the cyanine compound, diimonium compound and quencher compound therein is excellent, and durability is good, acrylic resin and polyester resin are preferred.

[0048]

There is no particular limitation on the thickness of the layer comprising the cyanine compound, but from the viewpoint of near-infrared absorption properties and visible light transparency, it is preferably of the order of 0.1µm to 20µm. [0049]

-Diimonium compound-containing layer-

There is no particular limitation on the diimonium compound, but the compound represented by any one of formula (I) and (II) is suitable. [0050]

[Chemical Formula 20]

$$\begin{bmatrix} R_8^7 \\ R_9 \end{bmatrix} N - \begin{bmatrix} R_1^9 \\ R_{10} \end{bmatrix}^{2+} \cdot 2X$$
 (1)

$$\begin{bmatrix} R^{7} \\ R^{8} \end{bmatrix} N \longrightarrow \begin{bmatrix} N \\ R^{10} \end{bmatrix}^{2+} \cdot Y^{2-}$$
 (II)

[0051]

In the formulae (I) and (II), " $R^{7}$ " to " $R^{10}$ " are at least any one of an alkyl group, an aryl group, a group comprising an aromatic ring, a hydrogen atom and a halogen atom. " $X^{-}$ " is a monovalent anion, and " $Y^{2-}$ " is a divalent anion.

[0052]

In the formulae (I) and (II), the monovalent anion represented by "X-" may be a halogen ion such as I-, Cl-, Br- or F-, an inorganic acid ion such as  $NO_3$ -,  $BF_4$ -,  $PF_6$ -,  $ClO_4$ -,  $SbF_6$ -, an organic carboxylic acid ion such

as CH<sub>3</sub>COO-, CF<sub>3</sub>COO- or benzoic acid ion, an organic sulfonic acid ion such as CH<sub>3</sub>SO<sub>3</sub>-, CF<sub>3</sub>SO<sub>3</sub>-, benzenesulfonic acid ion or naphthalene sulfonic acid ion.
[0053]

In the formulae (I) and (II), the divalent anion represented by "Y<sup>2-"</sup> is preferably an aromatic sulfonic acid ion comprising two sulfonic acid groups, for example an ion such as naphthalene-1,5-disulfonic acid, R acid, G acid, H acid, benzoyl H acid (benzoyl bonded to the amino group of H acid), p-chlorobenzoyl H acid, p-toluenesulfonyl H acid, chloro H acid (amino group of H acid replaced by chlorine atom), chloroacetyl H acid, methanyl γ acid, 6-sulfonaphthyl-γ acid, C acid, ε acid, p-toluenesulfonyl R acid, naphthalene disulfonic acid derivatives such as naphthalene-1,6-disulfonic acid and 1-naphthol-4,8-disulfonic acid, carbonyl-J-acid, 4,4-diaminostilbene-2,2'-disulfonic acid, acid. naphthalic acid, naphthalene-2,3-dicarboxylic acid, diphenic acid, stilbene-4,4'-dicarboxylic acid, 6-sulfo-2-oxy-3-naphthoic acid, anthraguinone-1,8-disulfonic acid, 1,6-diaminoanthraguinone-2,7disulfonic acid, 2-(4-sulfophenyl)-6-aminobenzotriazol-5-sulfonic acid, 6-(3-methyl-5-pyrazolonyl)-naphthalene-1,3-disulfonic acid, 1-naphthol-6-(4-amino-3 sulfo) anilino-3-sulfonic acid, and the like. Among these, naphthalene disulfonic acid ion is preferred, the ion represented by the formula (III) being particularly preferred. [0054]

[Chemical Formula 21]

$$\begin{array}{c|c}
R^{11} \\
12 \\
\hline
\end{array}$$

$$(SO_3^-)_2 \quad (|||)$$

[0055]

In the formula (III), " $R^{11}$ " and " $R^{12}$ " are at least any one of a lower alkyl group, hydroxyl group, alkylamino group, amino group, -NHCOR<sup>13</sup>, -NHSO<sub>2</sub>R<sup>13</sup> and -OSO<sub>2</sub>R<sup>13</sup> (wherein " $R^{13}$ " represents at least any one of an aryl and alkyl group. " $R^{13}$ " may comprise a substituent), acetyl group, hydrogen atom and halogen atom. [0056]

The above-mentioned diimonium compound may be preferably the compound represented by the formula (IV).

#### [0057] [Chemical Formula 22]

[0058]

In the formula (IV), "R" is an alkyl group having 1 to 8 carbon atoms, n-butyl being particularly preferred. "X-" may be preferably BF<sub>4</sub>,  $PF_{6}$ ,  $ClO_4$  or  $SbF_{6}$ . A preferred example of this diimonium compound is shown by the formula (V). [0059]

#### [Chemical Formula 23]

$$\begin{bmatrix}
C_{4}H_{9} \\
C_{4}H_{9}
\end{bmatrix}$$

$$C_{4}H_{9}$$

$$C$$

[0060]

The layer comprising the diimonium compound may comprise various other components if desired. As these other components, the above-mentioned quencher compound is particularly preferred from the viewpoint that it more conveniently prevents oxidation of the diimonium compound and allows a near-infrared absorption film having excellent durability to be obtained. Specific examples of the quencher compound are completely identical to those described above. Among quencher compounds, from the viewpoint of durability improvement, quencher compounds represented by the formula (5) is preferred, and among

quencher compounds represented by the formula (5), quencher compounds represented by the formula (8) and the formula (9) are more preferred, and quencher compounds represented by the formula (9) are particularly preferred.

The other components contained in the layer comprising the diimonium compound may be completely identical to those mentioned in "other components contained in the layer comprising the cyanine compound".

[0061]

There is no particular limitation on the thickness of the layer comprising the diimonium compound, but from the viewpoint of near-infrared absorption properties and visible light transparency, it is preferably of the order of  $0.1\mu m$  to  $20\mu m$ .

[0062]

[Transparent substrate]

There is no particular limitation on the material of the transparent substrate, which may for example be a resin of polyolefine, e.g., polyethylene or polypropylene, a resin of polyester, acrylic, cellulose, polyvinyl chloride, polycarbonate, phenolic or urethane, and the like. Among these, polyester resin is particularly preferred in respect of transparency and environmental robustness.

[0063]

There is no particular limitation on the thickness of the transparent substrate, but from the viewpoints of mechanical strength and thinness, it is preferably of the order of  $50\mu m$  to  $200\mu m$ . [0064]

[Manufacture of near-infrared absorption film]

There is no particular limitation on the method of manufacturing the near-infrared absorption film, for example, a coating solution obtained by dissolving the cyanine compound and a binder resin in a predetermined solvent, and a coating solution obtained by dissolving the diimonium compound and a binder resin in a predetermined solvent, may each be prepared, and coated on the transparent substrate. The predetermined solvent may for example be dichloromethane, methyl ethyl ketone, tetrahydrofuran, cyclohexanone, and the like. [0065]

[Composition of near-infrared absorption film]

There is no particular limitation on the composition of the

near-infrared absorption film provided that the near-infrared absorption layer comprises a layer comprising the above-mentioned cyanine compound and a layer comprising the above-mentioned diimonium compound, for example as shown in FIGs. 1 (1) to (4). [0066]

FIGs. 1 (1) to (4) are schematic diagrams showing a cross-section of the near-infrared absorption film in the present invention. In FIG. 1 (1), near-infrared absorption film 10 comprises layer 2 comprising a cyanine compound and layer 3 comprising a diimonium compound on the two surfaces of transparent substrate 1. In FIG. 1 (2), near-infrared absorption film 10' comprises layer 3' comprising a diimonium compound and layer 2' comprising a cyanine compound on transparent substrate 1' in that order. In FIG. 1 (3), near-infrared absorption film 10" comprises layer 2" comprising a cyanine compound and layer 3" comprising a diimonium compound on transparent substrate 1" in that order. In FIG. 1 (4), a near-infrared absorption film 10" comprises layer 2" comprising a cyanine compound, transparent substrate 1" and layer 3" comprising a diimonium compound on transparent substrate 1" in that order.

[0067]

[Examples]

The present invention will now be described by means of specific examples, but it should be understood that the present invention is not be construed as being limited in any way thereby.

[0068]

(Examples 1 to 4, Comparative Examples 1 to 2)

-Manufacture of near-infrared absorption film-

The "near-infrared absorption agents" and "binder resins" shown in the "first layer" in the Examples and Comparative Examples of Tables 1 and 2 were dissolved in a mixed solvent comprising 18.5g dichloromethane, 55.5g methyl ethyl ketone and 18.5g cyclohexanone to prepare a coating solution. The coating solution obtained was coated on a polyester film (transparent substrate) of width 200mm and thickness 100µm, and the coating was dried at 100°C for 3 minutes to form a first layer (thickness: 5µm) on the transparent substrate surface.

Next, the "near-infrared absorption agents" and "binder resins" shown in the "second layer" in the Examples and Comparative Examples of Tables 1 and 2 were dissolved in a mixed solvent comprising 18.5g

dichloromethane, 55.5g tetrahydrofuran and 18.5g cyclohexanone to prepare a coating solution. The coating solution obtained was coated on the opposite surface of the transparent substrate to that on which the first layer was formed, and the coating was dried at  $100^{\circ}$ C for 3 minutes to form a second layer (thickness: 5µm). In this way, a near-infrared absorption film was manufactured.

The infrared absorption film obtained was evaluated together with a film adjusted by red dye (BRDOU) and blue dye (Sumitomo Chemical Company Limited manufactured BLUE-S) so that the chromaticity (X, Y) was (0.310, 0.316).

[0069]

(Comparative Examples 3 to 4)

-Manufacture of near-infrared absorption film-

The "near-infrared absorption agents" and "binder resins" shown in the Comparative Examples of Table 2 were dissolved in a mixed solvent comprising 18.5g dichloromethane, 55.5g methyl ethyl ketone and 18.5g cyclohexanone to prepare a coating solution. The coating solution obtained was coated on a polyester film (transparent substrate) of width 200mm and thickness  $100\mu m$ , and the coating was dried at  $100^{\circ} C$  for 3 minutes to form a near-infrared absorption layer (thickness:  $10\mu m$ ) on the transparent substrate surface. In this way, a near-infrared absorption film was manufactured.

The infrared absorption film obtained was evaluated together with a film adjusted by red dye (BRDOU) and blue dye (Sumitomo Chemical Company Limited manufactured BLUE-S) so that the chromaticity (X, Y) was (0.310, 0.316).

[0070]

[Table 1]

F1.		Near infrared absorp	tion ager	Binder resin			
Example No.	Layer	Compound name	Product name	g	Compound name	Product name	g
	1st	Cyanine compound NK29		0.065	Polyester	UE3690	7.5
Ex. 1	layer	Quencher (metal complex)	MIR101	0.03	l	OE3090	7.5
EX. I	2 <sup>nd</sup>	Diimonium compound	CIR1081	0.48	Polyester	UE3690	7.5
	layer	Quencher (metal complex)	EST5	0.02	l	013090	/.5
	1st	Cyanine compound	NK2911	0.065	Polyester	UE3690	7.5
Ex. 1	layer	Quencher (aminium)	CIR960	0.025	l		
EX. I	2nd	Diimonium compound	CIR1081	0.48	Polyester	UE3690	7.5
	layer	Quencher (metal complex)	EST5	0.02	l	CESOSO	7.5
	1st	Cyanine compound	NK2911	0.063	Polymethylmethacrylate	80N	7.5
Ex. 3	layer	Quencher (metal complex)	MIR101	0.03	Orymentymientacrylate	0014	7.5
EX. 5	2 <sup>nd</sup>	Diimonium compound	CIR1081	0.48	Polymethylmethacrylate	80N	7.5
	layer	Quencher (metal complex)	EST5	0.02	l orymetry mietraer y rate	0014	7.5
Ex. 4	1st	Cyanine compound	NK2911	0.063	Polymethylmethacrylate	80N	7.5
	layer	Quencher (aminium)	CIR960	0.024	Orymetry miediacry late	0014	,.5
	2 <sup>nd</sup>	Diimonium compound	CIR1081	0.48	Polymethylmethacrylate	80N	7.5
	layer	Quencher (metal complex)	EST5	0.02	l orymetry miediacry late		7.3

## [0071]

[Table 2]

Escample	Layer	Near infrared absorption ag	gent	Binder resin			
Example No.		Compound name	Product g		Compound name	Product name	g
Comp. Ex. 1	1 <sup>st</sup> layer	Cyanine compound	NK2911	0.065	Polyester	UE3690	7.5
	2 <sup>nd</sup> layer	Diimonium compound	CIR1081	0.48	Tolyester	0123090	
Comp. Ex. 2	1 <sup>st</sup> layer	Cyanine compound	NK2911	0.063	Polymethylmethacrylate	80N	7.5
	2 <sup>nd</sup> layer	Diimonium compound	CIR1081	0.48	rolymentylmentacrylate		
Comp. Ex. 3	-	Cyanine compound	NK2911	0.063		80N	7.5
		Quencher (metal complex)	MIR101	0.03	Polymethylmethacrylate		
		Diimonium compound	CIR1081	0.48			
Comp. Ex. 4	-	Cyanine compound	NK2911	0.063		80N	7.5
		Quencher (aminium)	CIR960	0.024	Polymethylmethacrylate		
		Diimonium compound	CIR1081	0.48			

# [0072]

In Tables 1 and 2, [CIR1081] is manufactured by Japan Carlit, Co. Ltd. ("X-" is SbF<sub>6</sub>-), [CIR960] is manufactured by Japan Carlit, Co. Ltd.

("X-" is ClO<sub>4</sub>-), [NK2911] is manufactured by Hayashibara Biochemical laboratories ("X-" is ClO<sub>4</sub>-), [MIR101] is manufactured by Midori Kagaku, Co. Ltd., [EST5] is manufactured by Sumitomo Seika Chemicals, Co. Ltd., [UE3690] is a polyester resin [Elitel UE3690] manufactured by Unitika Ltd., and [80N] is a polymethylmethacrylate resin [Delpet 80N] manufactured by Asahi Kasei Corporation. [0073]

<Evaluation>

-Evaluation of initial spectrophotometric properties-

The near-infrared absorption films obtained were subjected to spectral measurements using a spectrophotometer (U-4000, manufactured by Hitachi Instruments Service, Co. Ltd.). If no deterioration was observed for any pigment, the film was rated ○, and if deterioration was observed for any pigment, it was rated ×. Table 3 shows the results.

[0074]

-Measurement of near-infrared transmittance and visible light transparency-

On the obtained near-infrared absorption films, the near-infrared transmittance thereof, and the luminous transmittance thereof under a light source C were measured using a spectrophotometer (U-4000, manufactured by Hitachi Measuring Instruments).

If the luminous transmittance (%) was 70% or more, the film was rated ○, and if it was less than 70%, it was rated ×. For near-infrared transmittance (%), if the transmittances in the wavelength region of 800nm to 1,100nm were all less than 20%, the film was rated ×, and if the transmittance was 20% or more, the film was rated ×. Table 3 shows the results.

[0075]

-Durability test-

The near-infrared absorption films obtained were subjected to two durability tests, i.e., leaving the film at 80°C for 500 hours, and leaving the film under a carbon arc using a sunshine weather meter (Suga tester) at an irradiation intensity of 100W/m² for 24 hours. Subsequently, the durability (heat resistance and antioxidation properties) was evaluated according to the following evaluation criteria. Table 3 shows the results. [0076]

-- Durability test criteria--

- · very excellent durability ··· ⊙
- · excellent durability, no problem in practice ⋯○
- · inferior durability ···×

#### [0077]

#### [Table 3]

Example No.		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Comp.	Comp.	Comp.	Comp.	
					2274. 0		Ex. 1	Ex. 2	Ex. 3	Ex. 4
	800nm		17.9	18.7	18.6	19.4	19.3	19.9	18.6	19.4
	850nm		3.4	3.8	5. <i>7</i>	6.1	4.0	6.4	5.7	6.1
Near infrared	900nm		8.2	8.8	8.1	8.4	9.3	8.9	8.1	8.4
transmittance	950nm		4.1	4.1	4.6	4.5	4.3	4.8	4.6	4.5
(%)	1000nm		3.4	3.2	4.1	3.9	3.4	4.2	4.1	3.9
	1100nm		2.1	2.0	2.4	2.3	2.1	2.4	2.4	2.3
	MAX		17.9	18.7	18.6	19.4	19.3	19.9	18.6	19.4
Luminous trans	smittance (	%)	73.0	70.7	74.7	72.2	74.2	<i>7</i> 5.5	74.7	72.2
Channelinia X		x	0.310	0.310	0.310	0.310	0.310	0.310	0.310	0.310
Chromaticity		у	0.316	0.316	0.316	0.316	0.316	0.316	0.316	0.316
Visible light tra rating	nsmittance	2	0	0	0	0	0	0	0	0
Near infrared trating	ransmittan	ce	0	0	0	0	0	0	0	0
Initial spectrophotometric properties rating		0	0	0	0	0	0	0	0	
Durability ratir	ıg		0	0	0	0	×	×	×	×

[0078]

From Table 3, it is seen that in Examples 1 to 4, a near-infrared absorption film having excellent near-infrared blocking properties, visible light transparency, good initial spectrophotometric properties and excellent durability, was obtained.

### [0079]

#### [EFFECTS OF THE INVENTION]

According to the present invention, a near-infrared absorption film having an excellent near-infrared ray blocking performance and visible light transparency, an excellent tone, and durability such as anti-deterioration properties can be provided.

# [BRIEF DESCRIPTION OF THE DRAWINGS] [FIG. 1]

FIGs. 1 (1) to (4) are schematic block diagrams showing a cross-section of a near-infrared absorption film of the present invention.

#### [DESCRIPTION OF THE REFERENCE NUMERALS]

- 1 ····· transparent substrate
- 1' ···· transparent substrate
- 1" ···· transparent substrate
- 1"" ··· transparent substrate
- 2 ······layer comprising cyanine compound
- 2' ····· layer comprising cyanine compound
- 2" ···· layer comprising cyanine compound
- 2" ··· layer comprising cyanine compound
- 3 ······ layer comprising diimonium compound
- 3' ····· layer comprising diimonium compound
- 3" ···· layer comprising diimonium compound
- 3" ··· layer comprising diimonium compound
- 10 ···· near-infrared absorption film
- 10' ···· near-infrared absorption film
- 10" ···· near-infrared absorption film
- 10" ··· near-infrared absorption film

# [DOCUMENT NAME] [FIG. 1] Drawing 10 10' 2 2' 1 3' 3 (1) (2) 10''' 10' ' 3'' (4) (3)

[DOCUMENT NAME] Abstract of Disclosure [ABSTRACT]

[PROBLEM TO BE SOLVED] The present invention provides a near-infrared absorption film having an excellent near-infrared ray blocking performance and visible light transparency, an excellent tone, and durability such as anti-deterioration properties.

[SOLVING MEANS] A near-infrared absorption film comprises a transparent substrate, and a near-infrared absorption layer which comprises a layer comprising a cyanine compound represented by the formula (1) and a layer comprising a diimonium compound. It is preferable that "A" is an embodiment represented by at least any one of formulae (2) to (4), and the near-infrared absorption layer is an embodiment comprising a quencher compound.

Formula (1)

[Chemical Formula 1]

In formula (1), "A" is a divalent bonding group comprising an ethylene group. " $R^{1}$ " and " $R^{2}$ " are monovalent groups comprising carbon atoms. "X-" is a monovalent anion.

[Chemical Formula 2]

$$-(CH = C)_3$$
,  $-CH = CH$   $-CH = CH$  Formula (2) Formula (3) Formula (4)

In formulae (2) to (4), "Y" is any one of an alkyl group, diphenylamino group, halogen atom and hydrogen atom.

[SELECTED DRAWINGS] None